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High precision determinations of $^{87}Rb/^{85}Rb$ in geologic materials by MC-ICP-MS

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Abstract

In comparison to thermal ionization mass spectrometry (TIMS), multiple collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) is better suited to obtain precise measurements of isotope ratios for elements that have only two stable isotopes such as Rb. The instrumental mass bias of Rb is corrected with admixed Zr following Waight et al. [T. Waight, J. Baker, B. Willigers, Chem. Geol. 186 (1–2) (2002) 99]. The technique presented here uses the $^{92}Zr/^{90}Zr$ for mass bias correction of the $^{87}Rb/^{85}Rb$ on the Micromass *IsoProbe* MC-ICP-MS. For an assumed $^{92}Zr/^{90}Zr$ value of 0.33339, a $^{87}Rb/^{85}Rb$ of 0.38554 ± 30 (2 S.D.) is obtained for the NBS-984 Rb standard solution over the course of 1 year. This value agrees with the presently accepted IUPAC ratio obtained from TIMS measurements. Within single analytical sessions, the reproducibility of $^{87}Rb/^{85}Rb$ measurements is 0.02–0.05% (2 S.D.). Consequently, this technique provides up to a 10-fold improvement in precision over conventional TIMS techniques, potentially enabling the detection of isotope fractionation effects that possibly occur during geologic and biologic processes. In addition, the technique is applicable for high precision Rb–Sr geochronology, potentially yielding ages with an uncertainty of ±0.1% (2 S.D.).

Keywords: Rubidium isotopes; High precision measurements; MC-ICP-MS

1. Introduction

Under ideal conditions, the $^{87}Rb/^{85}Rb$ can be measured by thermal ionization mass spectrometry (TIMS) to within ±0.2% [1], but typical external reproducibility is more like ±1% (e.g., Ref. [2]), because the rapid fractionation of Rb isotopes cannot be corrected for during TIMS analyses. For conventional isotope measurements, the isotope fractionation that occurs during TIMS measurements can only be corrected if the element of interest has at least three isotopes, of which two must not be affected by radioactive decay such that their ratio is constant in all materials. In this case, the desired isotope ratio is usually corrected relative to an assumed value of the constant ratio of the element. Unfortunately, this method is not applicable to Rb, which has only two stable isotopes. The fractionation is therefore usually corrected relative to measurements of Rb standards, assuming that fractionation of standards and samples are similar. This assumption is not always valid, limiting the precision of $^{87}Rb/^{85}Rb$ measurements by TIMS. Total evaporation of the desired element, a technique first described in Ref. [3], may also be potentially applicable for Rb isotope measurements. Using the total evaporation technique fractionation effects cancel due to the complete integration of the signal for all isotopes (e.g., Ref. [4]). This technique has, e.g., produced Re isotope measurements that have a reported 2σ precision of ±0.1% [5].

The introduction of multiple collector-inductively coupled plasma source mass spectrometry (MC-ICP-MS) has led to significant improvements in the precision of isotope ratio measurements for many elements [6–8]. The plasma source of a MC-ICP-MS ionizes most elements with higher efficiency than thermal ionization sources, thus enabling

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measurements of ultra low element concentrations with higher precisions than achieved by TIMS measurements [7]. Taking advantage of the simultaneous ionization of all elements in an ICP source, a stable isotope ratio of one element can be used to monitor the mass bias of different isotope ratios of another element in a neighbouring mass range, where these isotopes are more or less equally fractionated (e.g., Ref. [9]). This mass bias can be approximated using the exponential law [8]. Using stable isotope ratios of a different element for mass bias correction has become a common technique when measuring the isotope ratio of elements that have only two isotopes (e.g., Refs. [9–11]) by MC-ICP-MS. This technique has been used to determine Lu concentrations by isotope dilution measurements using Re [10] or Yb [12] to correct for mass bias. External mass bias correction has also been applied to determine natural stable isotope fractionation (Ag for Cd [13], Zn for Cu isotope measurements [9]); in search for decay effects of extinct nuclides (Pd for Ag isotope measurements [14]), or for common Pb analyses using Tl [15] for mass bias correction. Following the study of by Waight et al. [2], we use Zr for mass bias correction of Rb isotopes. Earlier attempts at measuring ^{87}Rb/^{85}Rb for Rb–Sr chronology using a single collector ICP-MS achieved a reproducibility similar to that of TIMS analyses [16,17]. Waight et al. [2] reported an external reproducibility of $\leq$0.05% using a MC-ICP-MS and adding Zr to samples correct for the instrumentally induced mass bias of Rb.

The objective of the present study is to address instrument-dependent pitfalls and methodical subtleties and apply this method to natural samples to determine their Rb isotope compositions. We report Rb isotope measurements over a period of more than a year using a different type of mass spectrometer equipped with a collision cell and report an analytical method that differs from the method described by Waight et al. [2]. Furthermore, we apply the method of high resolution Rb isotope measurements to natural samples in a search for possible stable Rb isotope fractionation.

2. Experimental procedures

2.1. Reagents, sample selection, and preparation

Ultra-clean Millipore® water (18.2 MΩ cm) was used; HCl and HNO_3 were distilled in sub-boiling stills. Rubidium reference materials used in this study include Alpha-Aesar® and NBS-984 standard solutions. Zirconium Alpha-Aesar® standard solution was used for mass bias corrections of Rb isotope ratios.

To evaluate if the used technique is suitable for high resolution Rb isotope measurements, different standard materials having varying matrices and Rb/Sr were analyzed for their Rb isotopic compositions. These materials include a greywacke (IGDL-GD) and a granite (G1RF), both obtained from the GZG, Universität Göttingen, Germany, and an island arc basalt (S-11). Additionally, a synthetic element mixture containing alkali- and alkaline earth metals prepared from Alfa-Aesar® ICP standard solutions was measured to test for possible matrix effects on Rb isotope ratio determinations. This synthetic standard solution contains 20 ppb Rb, 200 ppb Zr, and 5 ppm each of Sr, Ca, Mg, Na, K, Gd, Mo, and Ba in 0.1 M HNO_3, because these elements may be present in the Rb cut obtained from ion exchange columns. Because the procedure used here should potentially be applicable to high resolution Rb–Sr chronology, high-Rb/Sr minerals, i.e., a Münster in-house mica standard and the NBS-607 K-fsp standard, were also analyzed. In addition, we analyzed two tektites from the Chesapeake Bay impact structure [18] and an impact melt from the Dellen impact structure [19]. These samples were analyzed to search for possible variations in the natural ^{87}Rb/^{85}Rb due to high temperature evaporation. These materials were potentially subject to kinetic isotope fractionation and might have Rb isotope compositions that differ from most natural samples.

Whole rocks were first crushed into small pieces in a steel mortar and subsequently powdered in an agate mill. The in-house mica standard was prepared by grinding large mica flakes in a steel disk mill and then sieving into different grain size fractions. Afterwards, mica flakes from the 125–250 μm size fraction were handpicked under a binocular microscope. To remove brittle mineral inclusions such as apatite, the mica separate was ground in an agate mortar, washed with acetone, and dried under a heat lamp. Impact melt and tektite samples were broken into fragments and fresh, unaltered pieces were handpicked under a microscope. Approximately 10 mg of clean mica separate was digested in a HF–HNO_3 acid mixture in Savillex® vials placed on a hot plate for 1 day at 120 °C. For whole rock analyses, ~100 mg of sample powder was dissolved in HF–HNO_3 and placed inside Parr Teflon® bombs at 200 °C for 1 day. After digestion, the samples were dried, re-dissolved in 1 ml 2.5 M HCl, and equilibrated for 1 day in closed vials at 120 °C.

2.2. Chemical separation of Rb

A two-column chemistry was used to separate Rb from the rock (or mineral) matrix. To obtain precise and accurate Rb isotope ratio measurements by ICP-MS, it is essential to eliminate isobaric interferences from other elements, in particular from ^{87}Sr, ^{92}Mo, and, ^{94}Mo, which interfere with ^{87}Rb, ^{92}Zr, and ^{94}Zr, respectively.

Before ion exchange chromatography, all samples were centrifuged in 1-ml plastic vials to avoid loading precipitates onto the resin. From the centrifuged and decanted sample solution, we assume a recovery of 100% of Rb as this is highly soluble in HCl. In the first separation step, the sample is loaded on a quartz glass column filled with 4 ml cation exchange resin (DOWEX AG-50W-X8, 100–200 mesh, resin). Rubidium is separated from the rock–mineral matrix on the cation exchange resin using 2.5 M HCl [20,21]. After passing 9 ml of 2.5 M HCl, Rb is eluted with an additional 3 ml of 2.5 M HCl. Concentrations of Mo in the samples

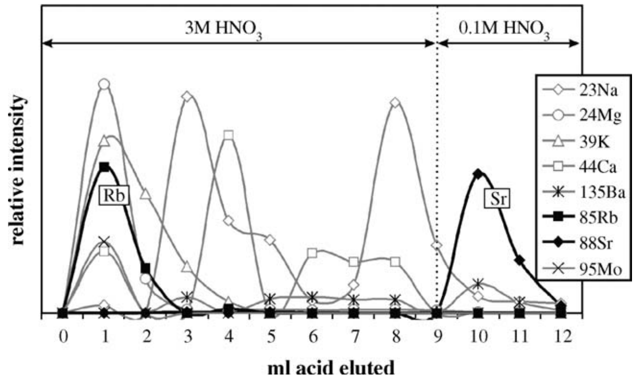

Fig. 1. Elution scheme for various elements on Eichrom Sr-Spec® resin. Total separation of Rb and Sr is achieved. For elements with a low atomic mass (i.e., <40), He (1.2 ml/min) instead of Ar was used in hexapole collision cell.

analyzed in this study are typically at the ppb level or below. The ^{95}Mo/^{90}Zr of the samples was typically 10^{-5} or lower, hence Mo interferences do not compromise the quality of the Rb-isotope ratios [22]. To eliminate the possibility of an isobaric inference from Sr on ^{87}Rb during MC-ICP-MS analyses, the Rb-separates were further purified with an additional cleaning step. For this cleaning step, we used Eichrom® Sr-Spec in Teflon® columns with a resin volume of ∼200 μl [23]. The best separation of Rb from Sr was achieved with 3 M HNO_3. All samples were dissolved in 1 ml of 3 M HNO_3, loaded onto the columns, and directly collected with one additional ml of 3 M HNO_3. This Rb cut contained more than 98% of the total Rb (Fig. 1), which was determined by yield tests with Rb standards that had undergone the same chemical separation technique. Owing to the high distribution coefficient of Sr in strong HNO_3 on Sr-Spec resin [15,23], it was possible to remove the Sr from the Rb cuts quantitatively. Although major elements from the rock matrix should have already been separated from the Rb cut during the first column procedure, remaining traces of these elements may cause matrix effects during Rb measurements that can lead to inaccurate measurements. Hence, we used a synthetic element mixture to test the separation of these elements from Rb with Sr-Spec resin. Fig. 1 shows the elution scheme for a solution containing 30 ppb Rb in a synthetic matrix that contains 15 ppb of Na + Sr + Ba + K + Mg + Ca separated on columns containing ∼200 μl of Sr-Spec resin. The results for Sr-Spec resin show that with 3 M HNO_3 only Mg, Ca, and K were found in the Rb cut. Testing with concentrations of up to 100 ppb of these elements added to the Rb standard solution with an unrealistically high element/Rb of five yielded indistinguishable Rb isotope ratios from the mean standard value. These elements therefore do not produce variations in the measured Rb isotope composition with the given concentrations. The trace amounts of Rb and matrix elements that remain adsorbed to the Sr-Spec resin can be washed off with ∼6 ml of 0.05 M HNO_3, which makes the resin reusable for Rb separation. We note, however, that for combined Rb and Sr separations, new resin should be used every time because significant amounts (∼50 ng) of Sr remain on the resin, even after five resin bed volumes of washout [23].

2.3. Data presentation and procedural Rb blanks

Uncertainties for all reported isotope ratios are at the 95% confidence level, where 2 S.E. (standard error) is defined as the internal run statistics error for a single sample analysis. The 2 S.D. (standard deviation, or by different users sometimes termed 2σ) is the external reproducibility, defined as the absolute deviation from the mean of all standards from a defined analytical period, which is typically an analytical session, if not stated differently. To express possible variations in the isotope composition of Rb, the deviation from the mean of NBS-984 reference value obtained for one measuring session is used. To express the deviation, the standard delta per mil notation is used:

$$\delta^{87}\mathrm{Rb}_{\text{NBS-984}} = \left[\frac{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}_{\text{sample}}}{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}_{\text{NBS-984}}} - 1\right] \times 10^3 \qquad (1)$$

Blanks were determined by isotope dilution using an ^{87}Rb-enriched tracer. Procedural Rb blanks were usually ≤30 pg. Because at least 30 ng of Rb are required for an analysis, the resulting sample/blank are typically ≥1000, rendering blank corrections insignificant.

3. Mass spectrometry

3.1. Instrument parameters and sample introduction

All Rb isotope measurements were preformed on a MC-ICP-MS, the Micromass *IsoProbe* at Münster. This single-focussing machine is equipped with one fixed and eight movable faraday collectors. The instrumental specifications of the *IsoProbe* are described in detail elsewhere (e.g., Ref. [7]). In the hexapole collision cell that serves as an energy filter [24], an Ar gas flow rate of 1.2 ml/min was used. Samples dissolved in ∼0.1 M HNO_3 were introduced into the mass spectrometer using a PFA Meinhardt microflow nebulizer and a water-cooled cyclonic spray chamber at a flow rate of 100 μl/min. This sample introduction system yields a lower sensitivity than desolvating nebulizer systems (e.g., the Cetac MCN-6000), but a much lower memory is achieved. Using an MCN introduction system, we observed a persistent Rb background of several mV on ^{85}Rb after several standard runs. Such Rb memory can significantly affect measurements of samples that contain variable amounts of an enriched isotope tracer. In contrast to the desolvating nebulizer, washout times for Rb in the cyclonic spray chamber were significantly shorter (<1 min instead of >5 min in the MCN) when using ∼0.2 M nitric acid. Depending on the concentration, Zr washout was less efficient than Rb but took no longer than 3 min. The washout of Zr is considered sufficient when the Zr signal is 0.1% of that measured during Rb analysis. This

Table 1
Possible interferences on Rb and Zr isotopes during MC-ICP-MS measurements

Rb measurements	
Isotope	
^{85}Rb	$^{170}Er^{++}$, $^{45}Sc^{40}Ar$, $^{50}Cr^{35}Cl$, $^{50}V^{35}Cl$, $^{48}Ti^{37}Cl$
^{87}Rb	^{87}Sr, $^{174}Yb^{++}$, $^{47}Ti^{40}Ar$, $^{71}Ga^{16}O$, $^{52}Cr^{35}Cl$, $^{40}Ar^{35}Cl^{12}C$
Zr measurements	
Isotope	
^{90}Zr	$^{180}Hf^{++}$, $^{50}Ti^{40}Ar$
^{91}Zr	$^{182}W^{++}$, $^{56}Fe^{35}Cl$, $^{40}Ar^{35}Cl^{16}O$, $^{91.1}X$ (organic)
^{92}Zr	^{92}Mo, $^{52}Cr^{40}Ar$
^{94}Zr	^{94}Mo, $^{40}Ar_2{}^{14}N$

Monatomic interferences of ^{87}Sr on ^{87}Rb and ^{94}Mo and ^{92}Mo on ^{94}Zr and ^{92}Zr were monitored with interference-free isotopes of the same element (^{88}Sr and ^{95}Mo), polyatomic interferences are negligible.

ensures that the mass bias correction on $^{87}Rb/^{85}Rb$ will not be affected by residual Zr in the instrument, which may be isotopically fractionated.

All measurements were performed in soft extraction mode, which results in a relatively low transmission compared to the hard extraction mode (e.g., Ref. [11]). In hard extraction mode, positive ions are accelerated by a negative voltage on the collimator cone. In soft extraction mode, however, a small positive voltage on the collimator reduces the ion velocity, which provides the advantage of reduced interferences from mono- or polyatomic ions (Table 1) that originate in the hexapole or interface region but results in a lower transmission. In practice, this somewhat lower sensitivity does not pose a problem for Rb measurements in geologic and geochronologic applications because sufficient amounts of Rb are available in most cases. Intensities of ~7 mV/ppb are typically achieved for NBS-984 Rb standard runs in soft extraction mode (22–25% extraction potential) with nickel cones. Similar intensities are possible with aluminium cones in soft extraction mode (9–12% extraction potential).

3.2. *Analysis conditions*

Rubidium has one of the lowest work functions of all elements, resulting in a very low ionization potential of 2.16 eV. Rubidium is thus easily ionized and produces stable beams during TIMS measurements. Because of its low work function, Rb deposited in the collector during measurements is readily ionized by impacts from other ions impinging on the collector. This re-ionized Rb can leave the collector, leading to an erroneous signal intensity in that collector. This results in incorrect isotope ratios, a situation that worsens with increasing amounts of Rb in the faraday cups. It is thus advisable to keep the amount of Rb introduced into the mass spectrometer to a minimum to prevent degradation of the Faraday cups. We therefore have restricted the measurements to a maximum intensity of ~300 mV for the most abundant Rb isotope.

To ensure the best reproducibility on the $^{87}Rb/^{85}Rb$, a minimum signal intensity of 40 mV on the least abundant Rb isotope (^{87}Rb for standard runs) must be achieved. Zirconium standard solution was added to all samples and standards, yielding a final concentration of ~600 ppb, which produces a ~800 mV signal for the most abundant isotope (^{90}Zr). As long as the standard solution concentrations resulted in at least 40 mV on ^{87}Rb and 200 mV on ^{90}Zr, no inaccurate fractionation correction effects were observed.

Data acquisition was performed in the static mode using three blocks of 20 cycles each with 5 s integration time. Baselines were measured before each block for 5 s at half masses above and below the peaks. No tail effects on half masses could be observed. Test runs with half masses measured below the Rb–Zr mass range yielded indistinguishable results for the Rb isotope composition in a single analytical session. This observation is in agreement with results reported for high precision Zr measurements on the *IsoProbe* [22].

3.3. *Interference and mass bias corrections*

All major interferences on Rb and Zr masses are listed in Table 1. The only isobaric interference on a Rb isotope is ^{87}Sr. This interference can be reduced by the chemical separation of Rb from Sr prior to ICP-MS measurements as described above. Any interference from remaining Sr can be corrected by monitoring ^{88}Sr. In natural samples, the $^{87}Sr/^{88}Sr$ is variable due to the decay of ^{87}Rb. As pointed out by Waight et al. [2], a ‘common’ $^{87}Sr/^{88}Sr$ composition for interference correction can, in theory, only serve as a first approximation. For a robust correction, the true $^{87}Sr/^{88}Sr$ must be determined by separate Sr isotope measurements. In practice, these corrections are minor, because the use of Sr-Spec resin leads to nearly complete removal of sample Sr from the Rb cut. Thus, a Sr isotope composition of $^{87}Sr/^{88}Sr$ of 0.085 [25] (corresponding to a $^{87}Sr/^{86}Sr$ of ~0.71) can be used for the interference correction. During the course of our measurements, we observed a typical $^{88}Sr/^{85}Rb$ of $1–4 \times 10^{-4}$ for the Rb NBS-984 standard. By applying the Sr-spec chemistry to natural samples, a similarly low Sr monitor was achieved. It is hence likely that the Sr originates from procedural reagent blanks, having a ‘common’ Sr isotope composition close to 0.71. Fig. 2A shows the variation in the mass bias- and interference-corrected $^{87}Rb/^{85}Rb$ with increasing amounts of Sr. We assumed a $^{87}Sr/^{88}Sr$ value of 0.085, which corresponds to a $^{87}Sr/^{86}Sr$ of 0.71. The Rb isotope composition obtained from the measurements shows a bias of ≤0.1% for $^{88}Sr/^{85}Rb$ values up to 4×10^{-3} (Fig. 2). For more radiogenic Sr having $^{87}Sr/^{88}Sr$ as high as 1 (corresponding to $^{87}Sr/^{86}Sr \cong 8$), an accuracy of 0.1% of the $^{87}Rb/^{85}Rb$ is still achieved when $^{88}Sr/^{85}Rb < 4 \times 10^{-4}$, which is the typical maximum value during the measurements in the study. Hence, even for samples that have extremely radiogenic Sr isotope compositions (e.g., old mica), the removal of Sr with Sr-Spec resin is sufficient to result in the accurate measurement of $^{87}Rb/^{85}Rb$. To correct for ^{92}Mo and ^{94}Mo interferences on ^{92}Zr and ^{94}Zr, ^{95}Mo is monitored during measurements and a $^{95}Mo/^{92}Mo$

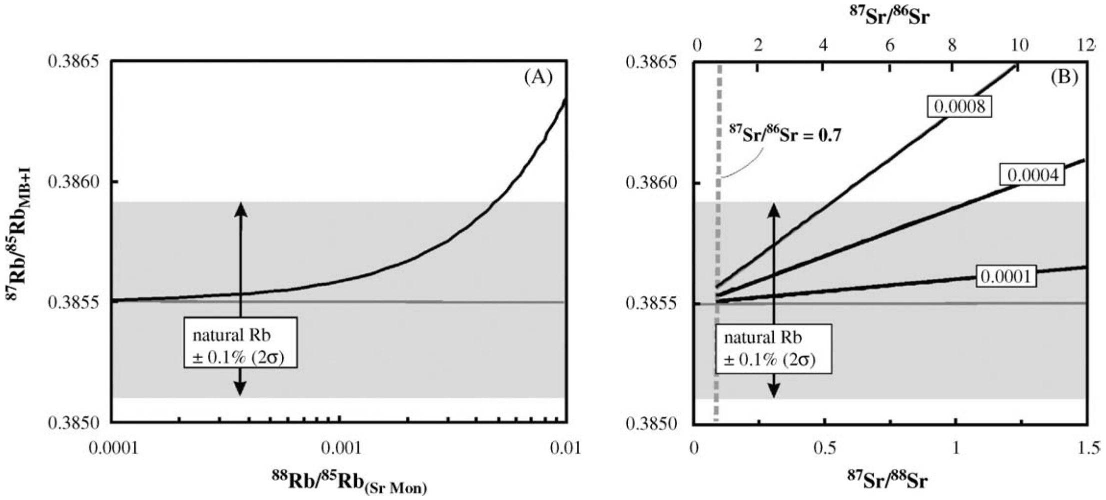

Fig. 2. (A) Effects on a mass bias- and interference-corrected (MB + I) ^{87}Rb/^{85}Rb of the NBS-984 standard as a function of variable amounts of admixed Sr as monitored by ^{88}Sr/^{85}Rb. For the interference correction of ^{87}Sr on ^{87}Rb, a ^{87}Sr/^{88}Sr of 0.085 was assumed. (B) ^{87}Rb/^{85}Rb$_{MB+I}$ as a function of increasing radiogenic ^{87}Sr in the sample at different values of ^{88}Sr/^{85}Rb (in boxes). The assumed ^{87}Sr/^{86}Sr and ^{87}Sr/^{88}Sr used for interference corrections in the present study are displayed for comparison (vertical dashed line).

of 0.93169 and a ^{95}Mo/^{94}Mo of 0.58018 are used [26] (see Table 2 for collector setup).

The instrumental mass bias for Rb isotopes in samples and standards, which is ∼3.5%/amu, was corrected online to the assumed Zr isotope composition of an admixed Zr Alpha-Aesar® standard solution. An interference on mass 91.1 was observed before most measurements and is probably an organic molecule (Fig. 3) with intensities of up to 40 mV. In most cases, it was possible to reduce or totally remove this interfering peak by baking the hexapole unit over night prior to the measurements (the hexapole unit is heated with halogen lights over night). Because another study carried out on a different type of MC-ICP-MS (Schönbächler et al. [27], p. 80) has also reported a 91.1 mass interference on ^{91}Zr, this feature is most likely not instrument-specific. As previously demonstrated for high precision Zr isotope measurements [28], remaining effects of this interference after a hexapole bakeout can be reduced to insignificant levels by a hard extraction bakeout of the interface (including the sampler and skimmer cones) prior to measurement. Here, the latter is heated by the plasma with the nebulizer gas off and the extraction lens at ∼70% in hard extraction mode for ∼30 min. For routine Rb isotope ratio measurements, the need for hard extraction bakeouts may be eliminated by using the interference-corrected ^{92}Zr/^{90}Zr or ^{94}Zr/^{90}Zr rather than ^{91}Zr/^{90}Zr for mass bias corrections.

Table 2
Collector configuration used for Zr and Rb measurements

Cup	Collector configuration							
	L3	L2	Axial	H1	H2	H3	H5	H6
Element	Atomic masses							
Rb	^{85}Rb	^{87}Rb						
Sr		^{87}Sr	^{88}Sr					
Zr				^{90}Zr	^{91}Zr	^{92}Zr	^{94}Zr	
Mo						^{92}Mo	^{94}Mo	^{95}Mo

For the present study, mass bias corrections were applied using the measured ^{92}Zr/^{90}Zr of admixed Zr and assuming that mass bias follows the exponential law such that $\beta^{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}}$ equals $\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$. The fractionation factor β is defined as

$$\beta = \frac{\ln\left(\frac{R_{\mathrm{true}}}{R_{\mathrm{measured}}}\right)}{\ln\left(\frac{M_1}{M_2}\right)} \qquad (2)$$

Here, R_{measured} is the isotope ratio of the respective element with R_{true} being an accepted value for this ratio relative to which all other isotope ratios of this element are reported. The mass of the numerator isotope is M_1 and the mass of the denominator isotope in the ratio is M_2. Although

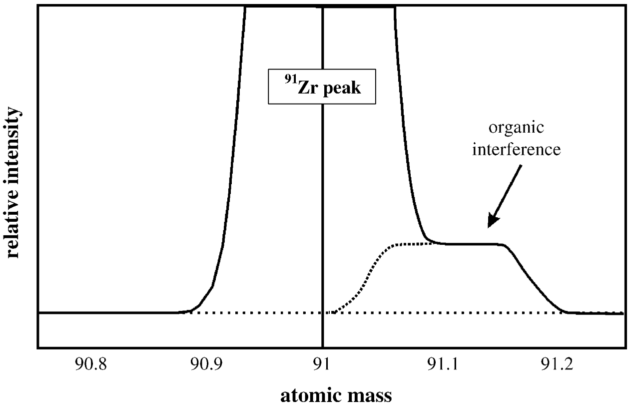

Fig. 3. Schematic illustration of the ^{91}Zr peak and an interfering mass at ∼91.1 of unknown origin.

the assumption of $\beta^{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}} = \beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$ (i.e., that the fractionation factors for neighbouring elements are equal) has been shown to be inadequate for applications that require extremely precise isotope ratios (e.g., ±0.005% [9,11]), it is sufficient for the Rb isotope dilution (ID) measurements used for Rb–Sr chronology where only 0.1% precision is required. Any errors introduced by the assumption of exponential law mass bias behaviour are insignificant, because isotope compositions of samples and standards would be systematically biased to similar extents. This bias would cancel when normalizing the ^{87}Rb/^{85}Rb of samples to the mean value of the Rb standard for the run session. This, however, requires that the matrix effects in sample analyses are insignificant. This was shown to be the case by testing several standard materials (e.g., granite, mica, K-fsp, and basalt) that have different matrices.

In a first step an online β-value for the ^{91}Zr/^{90}Zr is calculated:

$$\beta^{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}} = \frac{\ln\left(\frac{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}_{\mathrm{true}}}{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}_{\mathrm{measured}}}\right)}{\ln\left(\frac{M[^{91}\mathrm{Zr}]}{M[^{90}\mathrm{Zr}]}\right)} \tag{3}$$

This fractionation factor is used as a first approximation to apply a synthetic mass bias to the natural ^{92}Mo/^{95}Mo ratio:

$$^{92}\mathrm{Mo}/^{95}\mathrm{Mo}_{\mathrm{biased}} = \frac{^{92}\mathrm{Mo}/^{95}\mathrm{Mo}_{\mathrm{true}}}{\left(M[^{92}\mathrm{Mo}]/M[^{95}\mathrm{Mo}]\right)^{\beta^{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}}}} \tag{4}$$

which is then used for interference corrections of ^{92}Mo on ^{92}Zr:

$$\begin{aligned} &^{92}\mathrm{Zr}/^{90}\mathrm{Zr}_{\mathrm{IntCorr}} \\ &\quad = {}^{92}\Sigma/^{90}\mathrm{Zr} - \left[^{92}\mathrm{Mo}/^{95}\mathrm{Mo}_{\mathrm{biased}} \times {}^{95}\mathrm{Mo}/^{90}\mathrm{Zr}_{\mathrm{measured}}\right] \end{aligned} \tag{5}$$

The resulting interference-corrected ^{92}Zr/^{90}Zr$_{\mathrm{IntCorr}}$ from Eq. (5) can subsequently be used to provide an improved estimate of the β-value for Zr:

$$\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}} = \frac{\ln\left(\frac{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}_{\mathrm{true}}}{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}_{\mathrm{IntCorr}}}\right)}{\ln\left(\frac{M[^{92}\mathrm{Zr}]}{M[^{90}\mathrm{Zr}]}\right)} \tag{6}$$

The $\beta^{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}}$ was calculated using $^{91}\mathrm{Zr}/^{90}\mathrm{Zr} = 0.21795$ [22] and the $\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$ using $^{92}\mathrm{Zr}/^{90}\mathrm{Zr} = 0.33339$ [22]. In the same manner, a $\beta^{^{94}\mathrm{Zr}/^{90}\mathrm{Zr}}$ was obtained using the presently accepted value of 0.3381 [29] for ^{94}Zr/^{90}Zr. As in Eq. (3), the $\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$ is used to synthetically mass bias the assumed ^{87}Sr/^{88}Sr value of 0.085 to estimate the raw signal intensity of the ^{87}Sr to be subtracted from ^{87}Rb for the interference correction.

4. Results

4.1. Reproducibility

The method of using an isotope ratio of one element to correct the ICP-MS-induced mass bias of another element of similar mass has been successfully applied for high precision isotope measurements of many elements [9–11]. This technique generates reproducible and robust results if the two elements have a similar mass bias behaviour. In contrast to many of these element pairs, Rb and Zr are two elements that are drastically different in terms of ionic radius, charge, and ionization potential. It is therefore likely that the element-specific fractionation behaviours of Rb and Zr in a plasma source mass spectrometer differ. Measurements of a NBS-984 Rb standard solution performed between April 2004 to March 2005 show that assuming $\beta^{\mathrm{Rb}} = \beta^{\mathrm{Zr}}$ for Rb isotope mass bias corrections yields identical values for standards of various matrices when corrected to the ^{92}Zr/^{90}Zr, and a long-term reproducibility of ±0.078% (2 S.D.) for the ^{87}Rb/^{85}Rb of the NBS-984 standard. The reproducibility within individual analytical sessions is typically better, and a reproducibility of ±0.03–0.05% (2 S.D.) is readily achieved. Fig. 4 reports interference-corrected Rb versus Zr isotope ratios and $\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$ versus $\beta^{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}}$ for the all analyses of the NBS-984 standard made during this study. The standards form a linear array that is almost parallel to the one-to-one correlation predicted by the exponential law. Taking the range in Rb isotope ratios observed during the course of the study, the maximum deviation of the measured and assumed (by the applying exponential law) Rb isotope composition of the standard value has proven to be insignificant with respect to the external reproducibility.

Fig. 5 illustrates the effects of using different Zr isotope ratios (^{91}Zr/^{90}Zr, ^{92}Zr/^{90}Zr, and the ^{94}Zr/^{90}Zr) to correct the ^{87}Rb/^{85}Rb of NBS-984 standard runs for mass bias. Within a single analytical session, the mean values of ^{87}Rb/^{85}Rb obtained by normalizing to each of the three different Zr ratios are indistinguishable from each other. It is important to mention that the Zr ratios used in this study are internally consistent and reported relative to the ^{94}Zr/^{90}Zr of 0.3381 after Minster and Allègre [29]. Rubidium ratios corrected with $\beta^{^{91}\mathrm{Zr}/^{90}\mathrm{Zr}}$ appear to be systematically higher than Rb ratios corrected with $\beta^{^{92}\mathrm{Zr}/^{90}\mathrm{Zr}}$ and $\beta^{^{94}\mathrm{Zr}/^{90}\mathrm{Zr}}$, nevertheless ^{87}Rb/^{85}Rb values corrected to all three β-values overlap within errors and yield a reproducibility of 0.08% (^{91}Zr/^{90}Zr), 0.05% (^{92}Zr/^{90}Zr), and 0.06% (^{94}Zr/^{90}Zr) (2 S.D.), respectively, within a single analytical session. Although all ^{87}Rb/^{85}Rb values agree with the value recommended by the IUPAC [30], we prefer the value corrected to the ^{92}Zr/^{90}Zr because it is in excellent agreement with the value corrected to ^{94}Zr/^{90}Zr and provides the best external reproducibility within one analytical session, i.e., ±0.02–0.05%. This reproducibility was obtained for runs of samples spiked with an ^{87}Rb-enriched tracer that were run between standards.

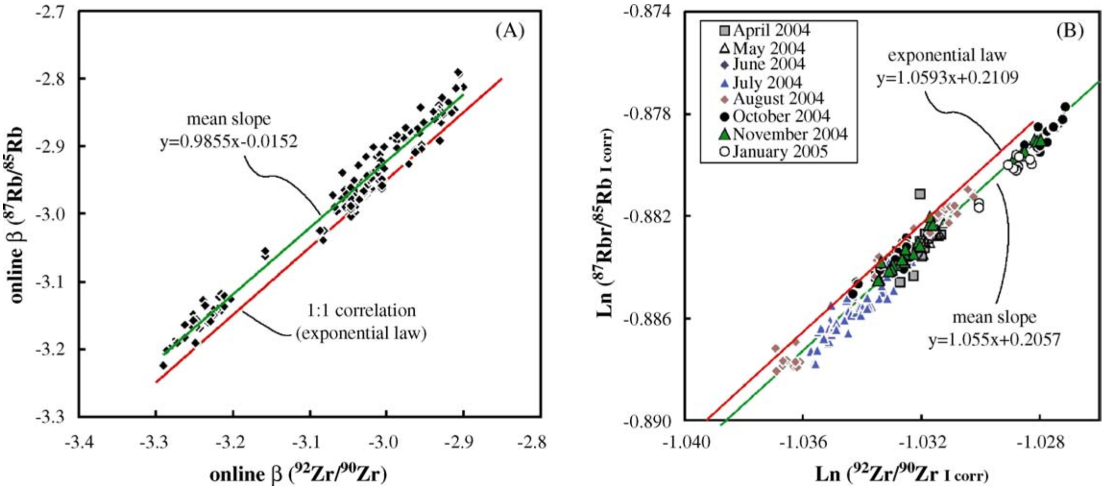

Fig. 4. Correlations between the Rb and Zr mass bias of all analyzed NBS-984 standard runs in this study. (A) The relation between β_{Rb} and β_{Zr}, which are measured simultaneously during Rb analyses. (B) The relationship between the natural logs interference-corrected Rb and Zr isotope ratios. Note that the mean slope is calculated from all analytical sessions.

4.2. Rubidium isotope compositions of natural samples

Fig. 6 illustrates the isotope compositions of the natural samples expressed in δ^{87}Rb. As demonstrated in the figure, the ^{87}Rb/^{85}Rb of the standard materials (i.e., mica, K-fsp, granite, greywacke, and basalt) agrees with the composition of the NBS-984 Rb standard. Therefore, none of these natural, terrestrial materials with different matrices show evidence for natural isotope fractionation effects. Furthermore, a NBS-984 standard solution that was run through the entire chemistry yielded an isotope composition identical to the mean NBS-984 standard value. From this, we infer that the assumption for non-radiogenic Sr in the Rb standards is most likely true and that no organic components which affect the measured isotope ratio of Rb were introduced by the chemistry. Additionally, there is probably no isotope fractionation occurring on the columns during chemical separation. Furthermore, measurements made with varying amounts of Mg, K (1–1000 ppb), and Sr (1–100 ppb) added to a 20 ppb Rb standard solution (i.e., Mg/Rb and K/Rb of 250 and a maximum Sr/Rb of 5) do not produce any significant change in the measured ^{87}Rb/^{85}Rb. The addition of Mo yields different Rb isotope ratios as the interference correction on Zr becomes inaccurate. At Mo/Zr of less than 0.1, sufficiently accurate Zr ratios were obtained (as previously demonstrated by Münker et al. [28]). However, the chemical separation presented in this study provides significantly cleaner Rb fractions and no Mo was observed during the natural sample runs. These features show that no matrix effects or column fractionation effects cause shifts in the measured isotope compositions of Rb and there are no apparent analytical mass fractionation effects. A variety of natural standard materials apparently has identical isotope compositions of Rb.

Significant natural isotope fractionation can be expected in impact melts, tektites or high temperature materials that have lost volatiles due to evaporation. However, earlier studies on the stable isotope composition of K [31] and Mg [24] did not reveal any mass dependent fractionation effects for impact

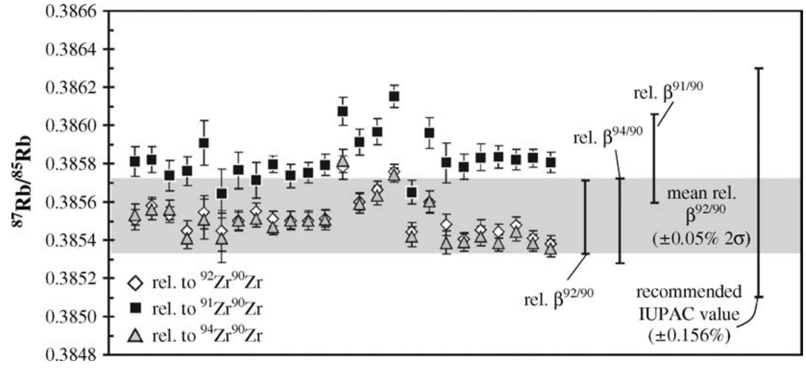

Fig. 5. Rb isotope composition of the NBS-984 standard solution showing the effect of using different ratios (^{91}Zr/^{90}Zr, ^{92}Zr/^{90}Zr, and the ^{94}Zr/^{90}Zr) to correct ^{87}Rb/^{85}Rb for mass bias. The data are from a single analytical session. Errors on individual measurements are 2 S.E.; error bars (2 S.D.) for mean ^{87}Rb/^{85}Rb relative to different β-values are shown on the right hand side.

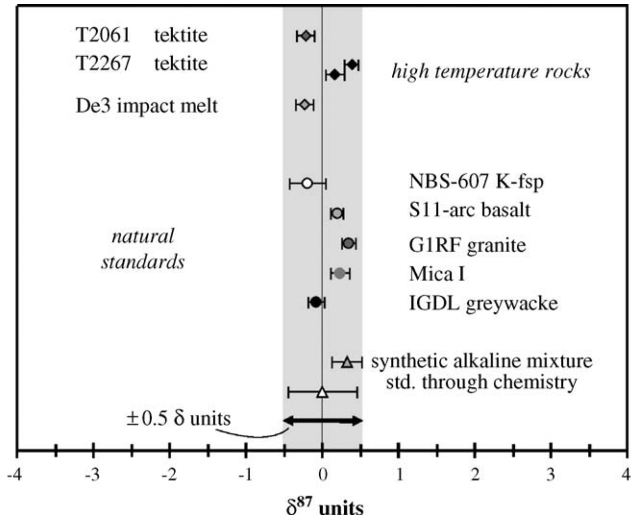

Fig. 6. Rb isotope composition of natural and synthetic samples expressed as δ^{87}Rb. All measured isotope ratios plot within the external 2 S.D. of the measurement session averages of the NBS-984 standard (i.e., ±0.5 δ units). Standards and samples were run under similar conditions. No anomalous isotope fractionation was observed for the samples. Errors on symbols are 2 S.E. (within-run errors).

rocks. Both elements represent lighter isotopes than Rb with a larger mass difference. In contrast, the highly volatile element Cd (which is heavier than Rb) shows significant isotope variations during tektite formation (e.g., Cd [11]). Hence, significant fractionation of the initial Rb may be expected in impact melts, tektites or high temperature phases as well.

Assuming an ideal Rayleigh fractionation, changes in the natural isotope composition of Rb (equivalent to that observed for Cd [13]) can be described with the equation,

$$\frac{(^{87}\mathrm{Rb}/^{85}\mathrm{Rb})_{\mathrm{residue}}}{(^{87}\mathrm{Rb}/^{85}\mathrm{Rb})_{\mathrm{initial}}} = f[\alpha_{\mathrm{kin}}^{-1}] \qquad (7)$$

where f is the mass fraction of the initial Rb and α_{kin} is the kinetic isotope fractionation factor defined by:

$$\alpha_{\mathrm{kin}} = \frac{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}_{\mathrm{vapor}}}{^{87}\mathrm{Rb}/^{85}\mathrm{Rb}_{\mathrm{residue}}} = \sqrt{\frac{M[^{87}\mathrm{Rb}]}{M[^{85}\mathrm{Rb}]}} = 1.01169 \qquad (8)$$

Thus, under equilibrium conditions, the ^{87}Rb/^{85}Rb of a vapour is elevated by at most 11.7 δ units over the residual solid phase. One impact melt from the Dellen impact structure (De3, Ref. [19]) and two tektites from the Chesapeake Bay impact structure (T8-2061 and T8-2267, Ref. [18]) were analyzed for their Rb isotope compositions. Within the analytical precision of ±0.5 δ^{87}Rb, none of these samples shows a Rb-isotope ratio that is distinguishable from the NBS-984 Rb standard (Fig. 6), which was taken as the initial reference value.

5. Conclusions

This study shows that high precision Rb isotope measurements can be achieved using the Micromass *IsoProbe* MC-ICP-MS following an efficient and clean chemical separation of Rb. The chemical separation of Rb from the rock or mineral matrix with a coupled two-column separation is adequate for high precision Rb isotope measurements and provides almost quantitative separation of Rb from isobarically interfering Sr. By using a standard cation chemistry with a DOWEX AG-50W-X8 resin combined with further purification of the Rb cut using Eichrom Sr-Spec®, no matrix effects from other elements could be observed during the analysis of natural samples.

It is demonstrated that Zr isotopes can be used to correct for the Rb mass bias with a reproducibility of ±0.05% or better for the NBS-984 Rb standard, despite the remarkably different physical properties of Rb and Zr. The most robust mass bias correction for Rb is achieved using the ^{92}Zr/^{90}Zr, however, all Rb isotope compositions obtained from different Zr isotope ratios used for mass bias corrections overlap within errors. Using ^{91}Zr/^{90}Zr for Rb isotope mass bias corrections on the *IsoProbe* can only be done if the interference at mass 91.1 is first eliminated by a hard extraction bake of the interface region. Long-term determinations of the ^{87}Rb/^{85}Rb corrected for mass bias with the exponential law and an assumed ^{92}Zr/^{90}Zr of 0.33339 indicate that the isotope composition of NBS-984 Rb standard can be reproduced within ±0.078% (2 S.D.). The absolute value of 0.38554 ± 30 is indistinguishable from the ^{87}Rb/^{85}Rb of 0.38540 ± 19 reported by Waight et al. [2], who used ^{91}Zr/^{90}Zr (with an assumed value that corresponds to Zr abundances used in this study) for mass fractionation correction using a different MC-ICP-MS and is in agreement with the value of 0.38570 ± 60 recommended by the IUPAC [30]. The Rb isotope composition obtained by MC-ICP-MS strongly depends on the natural Zr isotope composition used for mass bias correction and of the mass fractionation law itself. It is thus possible that errors on the natural Zr isotope composition lead to systematic errors in the absolute ^{87}Rb/^{85}Rb. It should be noted, however, that this error cancels by normalizing to the daily standard.

Within the analytical reproducibility of ±0.5 δ^{87}Rb, no natural variations in the Rb isotope compositions of terrestrial samples could be observed so far. Even rocks that were potentially subject to isotope fractionation (i.e., impact melts or tektites) do not show any variations. Hence, unless a higher resolution technique for the determination of Rb isotope compositions is developed, fractionation effects induced by terrestrial processes probably cannot be revealed. In addition to stable isotope measurements, this technique should also be applicable to high precision Rb–Sr geochronology [2,32], where Rb isotopes mixed with an isotope tracer can potentially be determined with a similar precision. An improved Rb–Sr chronometer would thus provide ages with a precision of ±0.1 % (2 S.D.) which is similar to the precision obtained for good U–Pb age determinations.

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